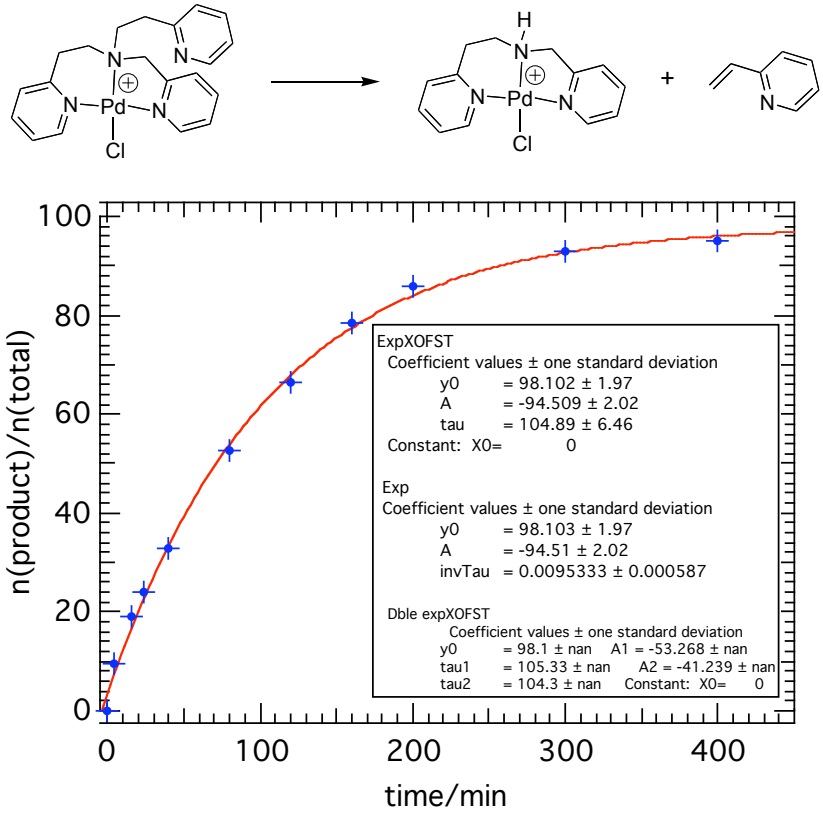
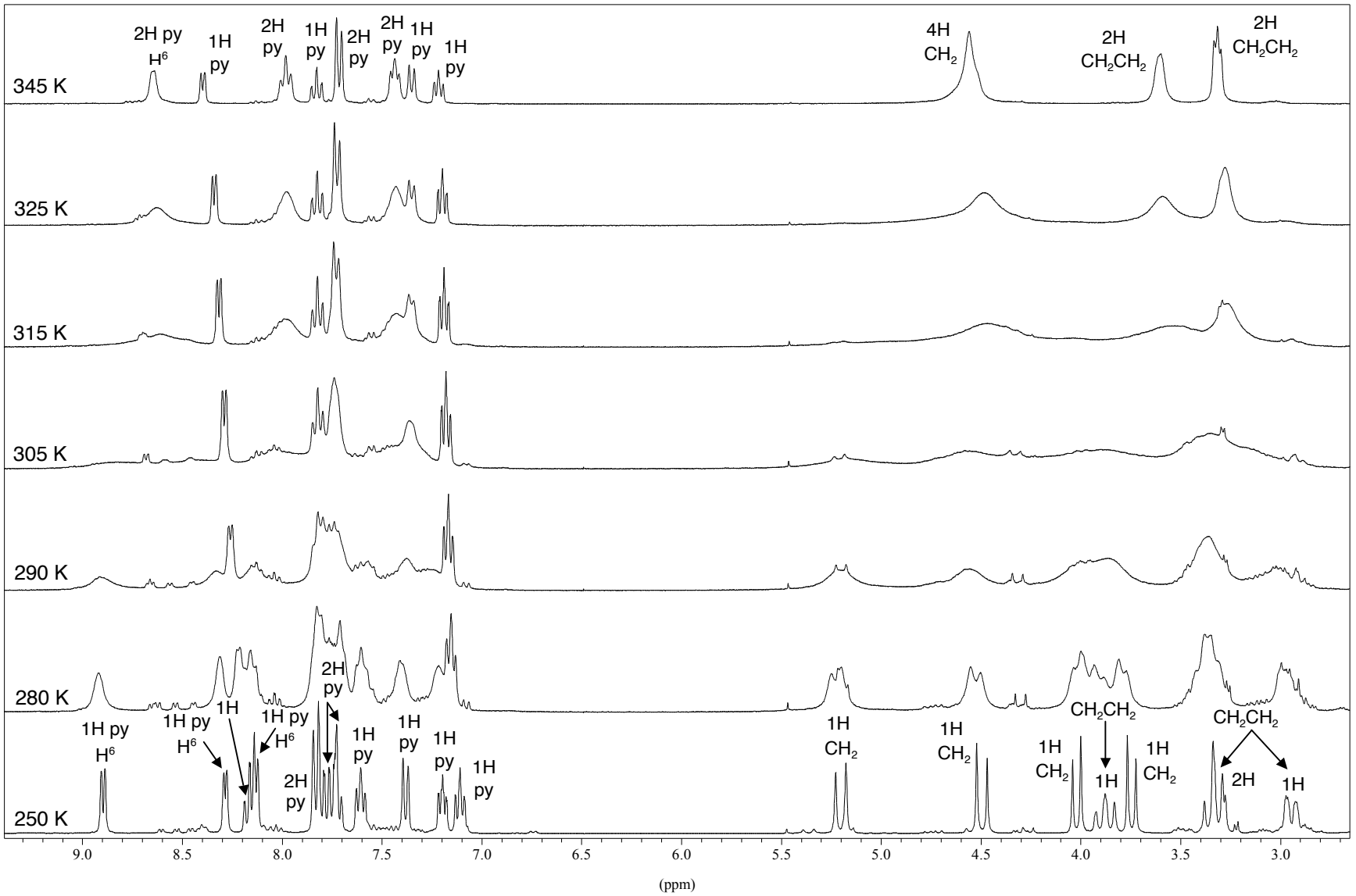
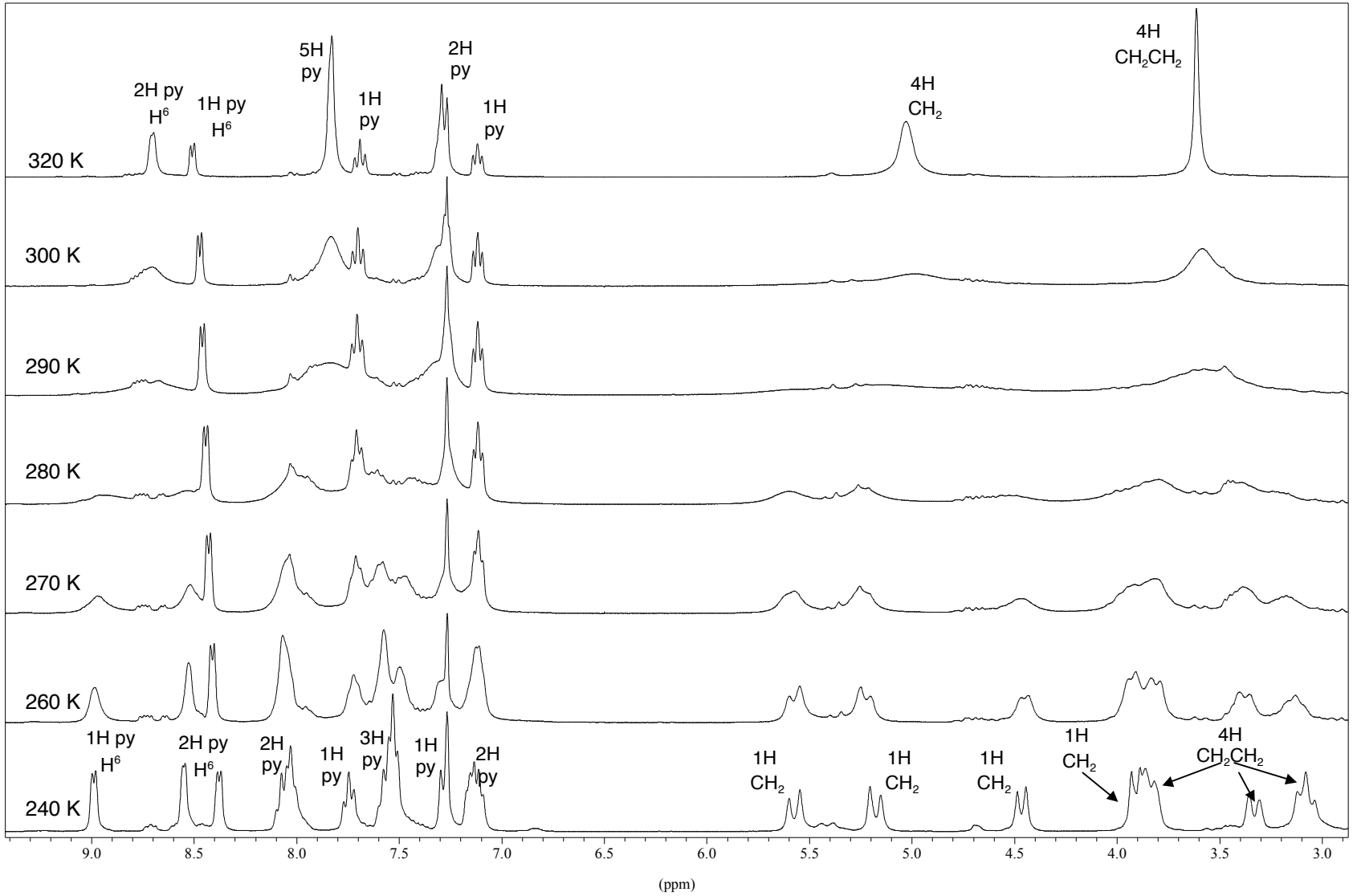
B. Additional NMR spectroscopy figures



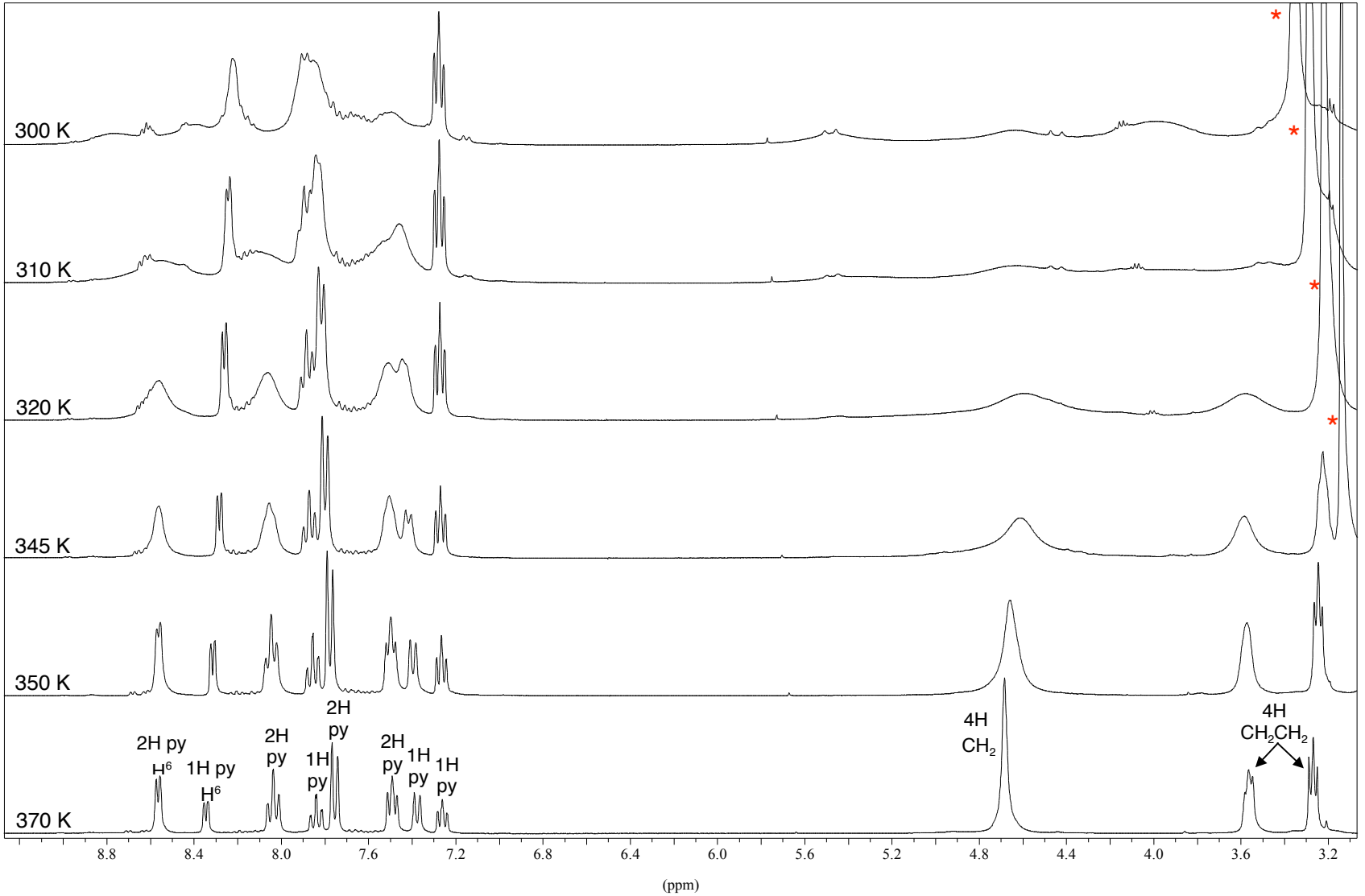
ESI Fig. B1. Plot of the %product against time for the conversion of $[Pd(pmap)Cl]^+$ to $[Pd(epmpa)Cl]^+$ at 390 K in d_6-dmso. The points are the experimental data from the 300 MHz ^1H NMR spectra shown in Figure 8 (in the paper) and the curve shows the fit of the data to a single exponential.



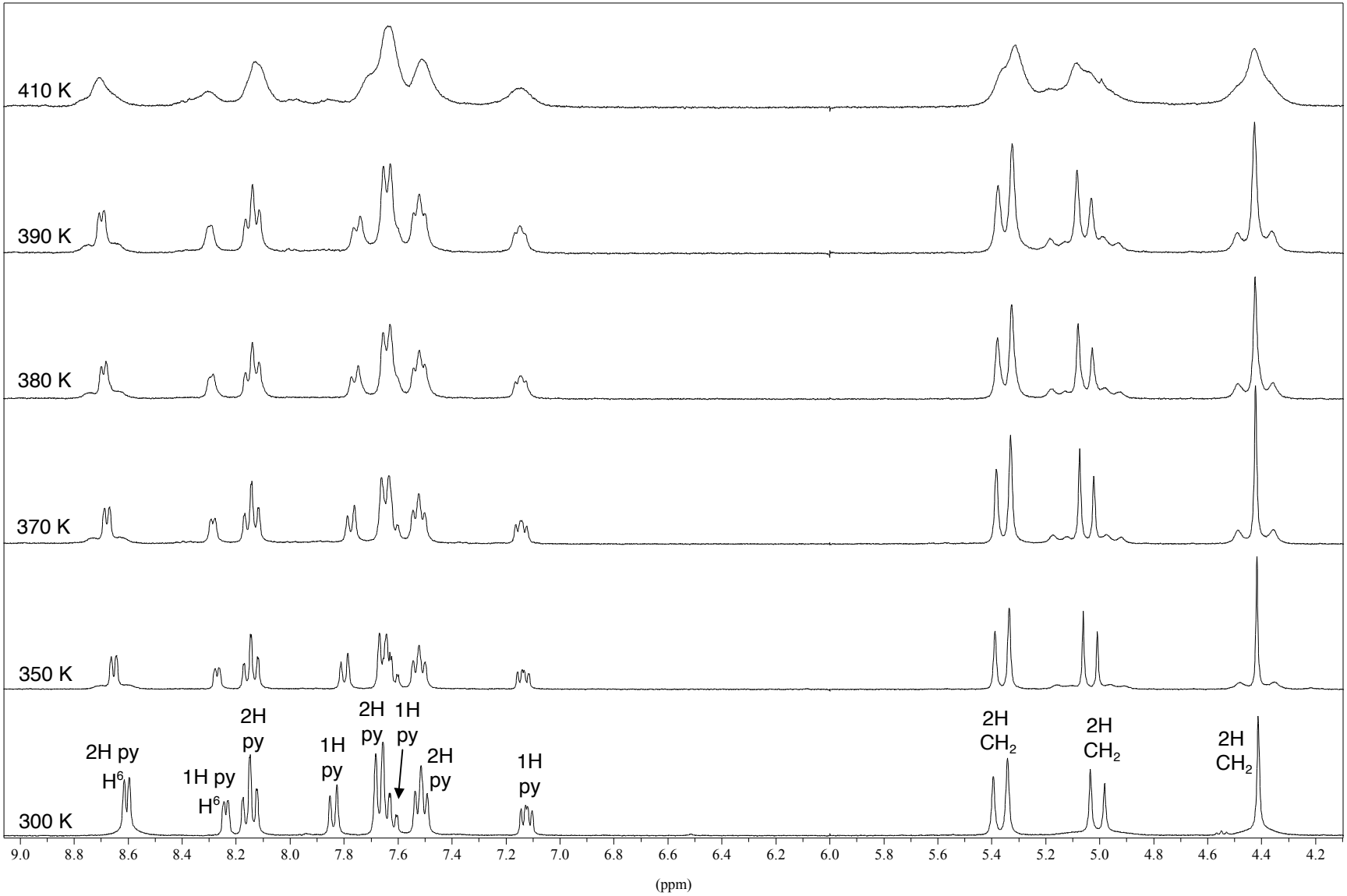
ESI Fig. B2: Variable temperature 300 MHz ^{1}H NMR spectra of [Pd(pmea)Cl]Cl in CD_3CN.



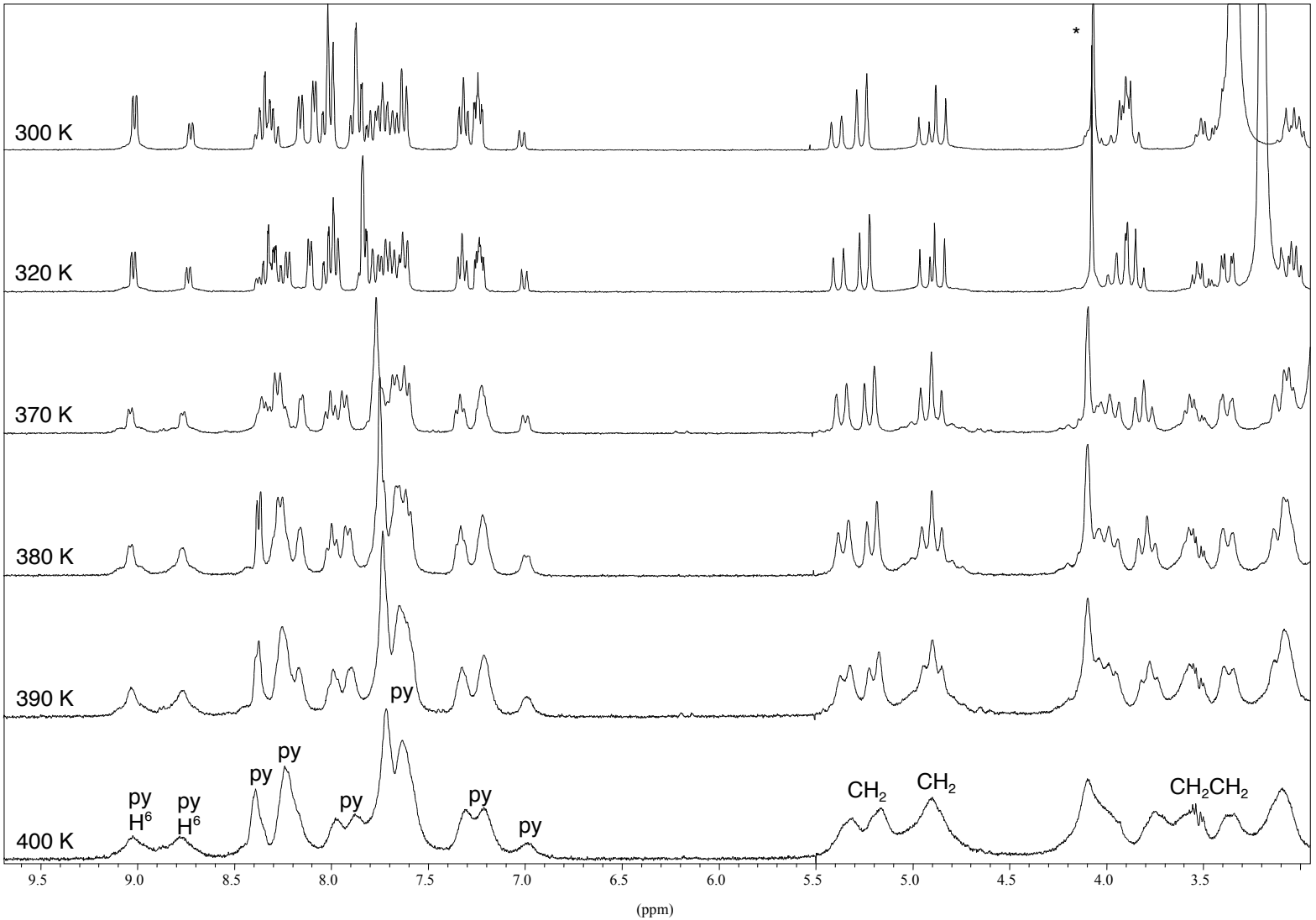
ESI Fig. B3: Variable temperature 300 MHz ^{1}H NMR spectra of [Pd(pmea)Cl]Cl in CD_3Cl.



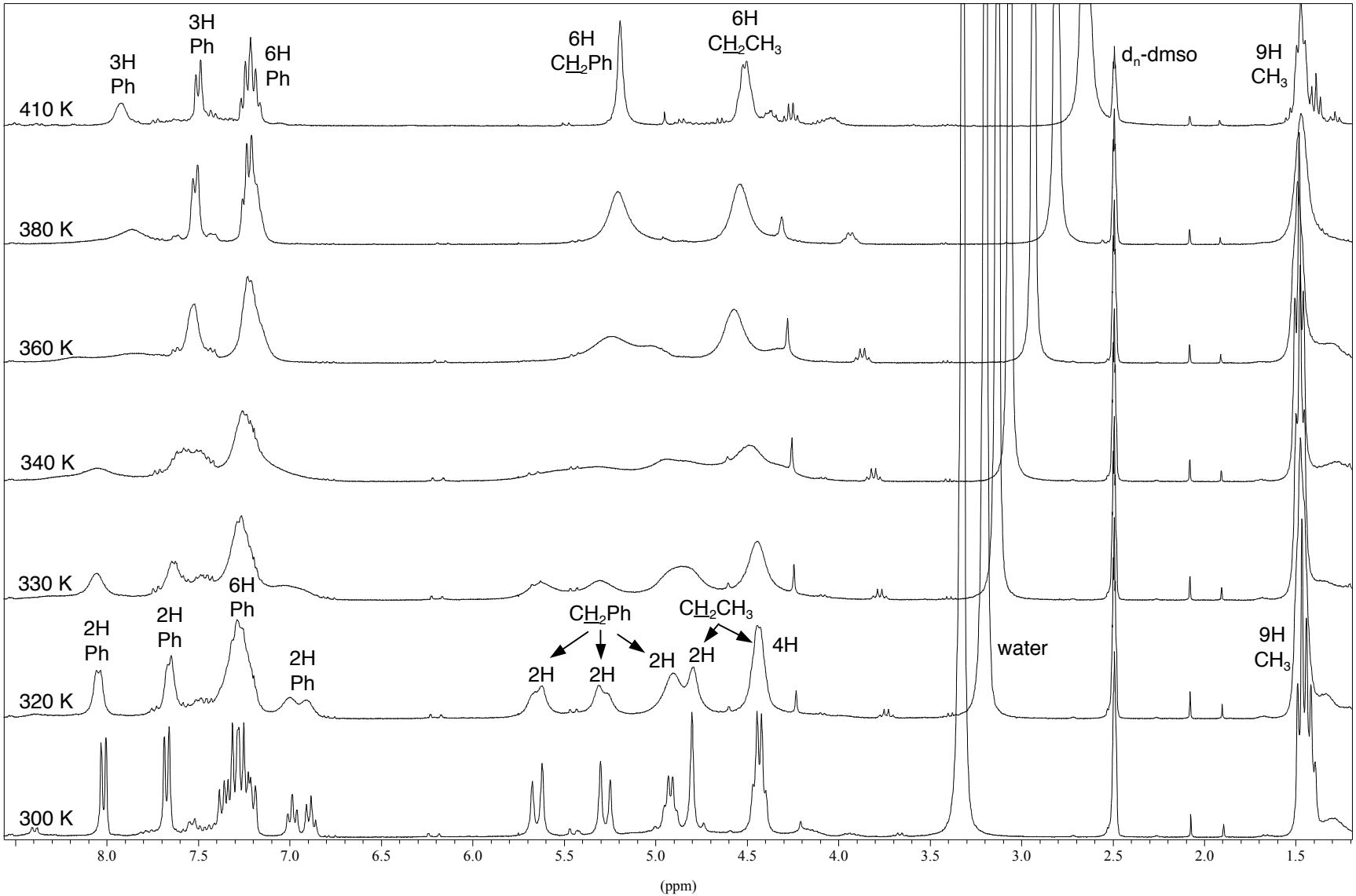
ESI Figure B4: 300 MHz variable temperature ^{1}H NMR spectra of [Pd(pmea)Cl]Cl in d_6-dmso (* denotes water). Note: The spectra in ESI Figs B2–B4 show peaks for only the asymmetric isomer with one bound and one dangling pyridylmethyl legs (see text of paper).



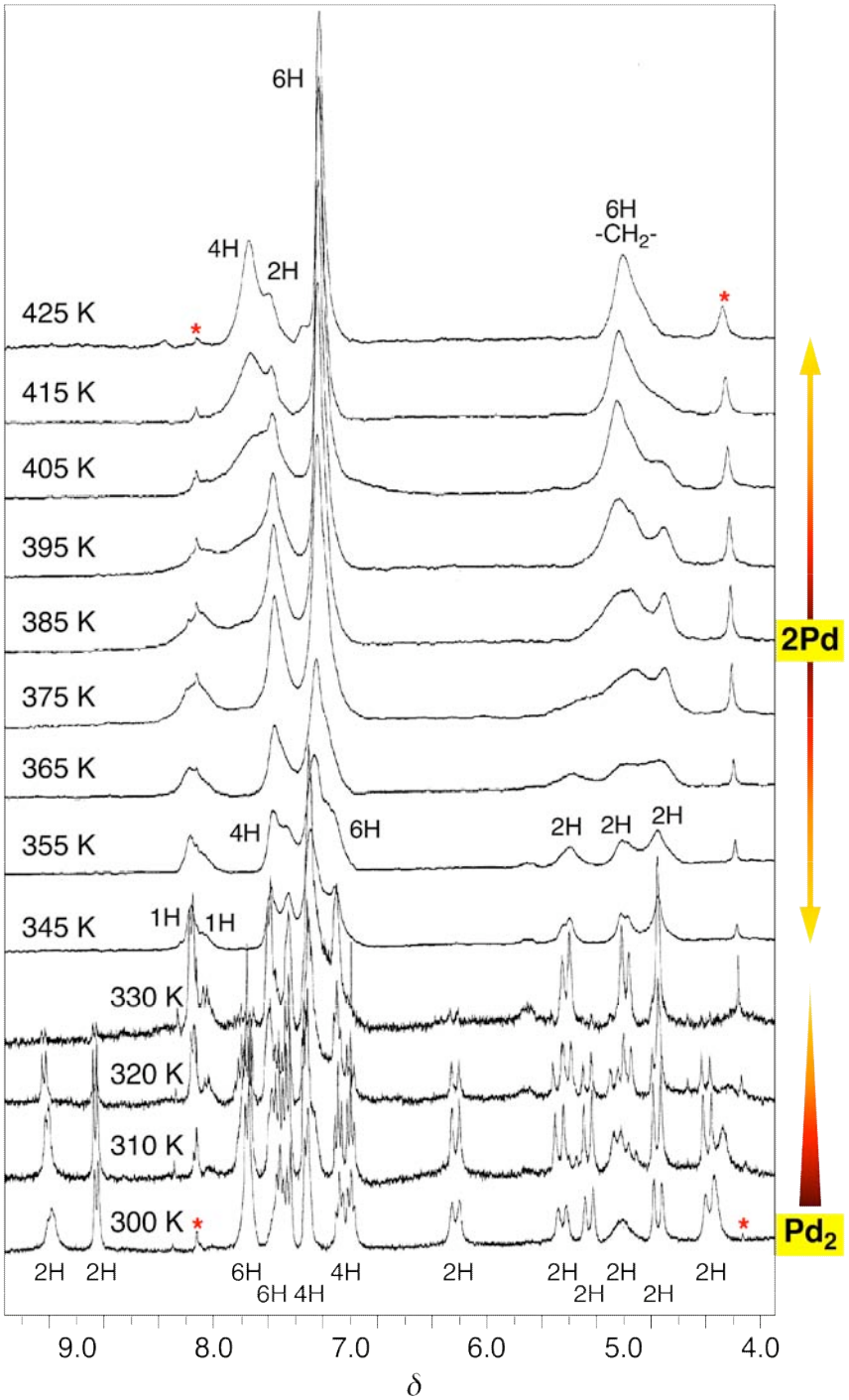
ESI Fig. B5: Variable temperature 300 MHz ^{1}H NMR spectra of [Pt(tmpa)Cl]Cl in d_6-dmso.



ESI Fig. B6: 300 MHz variable temperature ^{1}H NMR spectra of [Pt(pmea)Cl]Cl (two isomers — see text of the paper) in d_6-dmso. All changes were fully reversed upon cooling.



ESI Fig. B7: Variable temperature 300 MHz ^{1}H NMR spectra of [Pd(Et-tbima)Cl]Cl in d_6-dmso.



ESI Fig. B8. 300 MHz variable temperature ^{1}H NMR spectra for $[Pd(tbima)_2Cl]_2^{2+}$ in d_6-dmso solution. The first four spectra (from the bottom) show the clean break-up of the dimer (36 protons) to afford the monomer, $[Pd(tbima)Cl]^+$ (18 protons). The subsequent nine spectra show the changes in the NMR spectrum of the monmeric cation at increasingly higher temperatures; all changes in the latter nine spectra were completely reversed on cooling (* denotes a peak for an impurity).